A new Spectrophotometric Method For The Determination of La (III) With 3-Hydroxy -4-(2-hydroxy-Phenyl azo) Naphthalene -1- Sulfonic Acid

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Abstract

A simple, rapid and sensitive spectrophotometric method has been proposed for the determination of La (III) using 3-hydroxy -4-(2-hydroxy-phenyl azo) naphthalene -1- sulfonic acid as a chromogenic reagent. This method is based on the formation of a red-pink colored complex, upon the reaction of La(III) with the reagent in an alkaline medium (pH= 9.50), having a maximum absorbance at 459 nm. Beer's law is valid in the concentration range 0.5-12 $\mu g.ml^{-1}$ with a Sandell's sensitivity value of 0.0188 $\mu g.cm^{-2}$ and molar absorptivity of 7376.12 $L.mol^{-1}.cm^{-1}$. The stoichiometric composition of the chelate is 1:3. The effect of the presence of different cations as interferants in the determination of La(III) under the given optimum conditions were investigated.

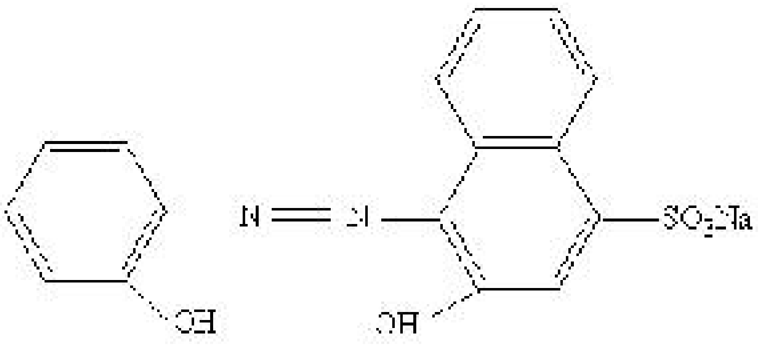
Key words :Spectrophotmetric , Determination of La (III) ,3-Hydroxy -4-(2-hydroxy-Phenyl azo) Naphthalene -1- Sulfonic Acid

Introduction

A basic characteristic of the lanthanide group is the chemical similarity of individual members. Consequently, data on the total lanthanide content often suffer in practical problems, particulary when all the lanthanides behave similary, such as the production of alloy steel or when the ratio of the individual members is constant as in geochemistry.[1] Lanthanum and its compounds are used in high technology applications, such as superconductors, supermagnets, nuclear chemistry, laser, alloy and also as anticoagulants[2]. Various methods such as isotopic dilution mass spectrometry (ID-MS)[3], instrumental neutron activation analysis (INAA)[4], inductively coupled plasma mass spectrometry (ICD-MS)[5], and inductively coupled plasma atomic emission spectrometry (ICPAES)[6,7] are available for the determination of La . These methods require costly equipments or a reactor facilities for (INAA); most of the laboratories are not equipped with these instruments, interest.

Azo dyes are a very important class of organic compounds receiving attention in the scientific literature. Recently, azo metal chelates have drawn the attention of some research due to their excellence in sensitivity and stability as optical recording medium[8,9]. Moreover, the complexes of some azo dyes with metal ions, such as Co(II), Ni(II), Zn(II) and Pd(II) have been recently investigated as recording materials for DVD-R (Digital Versatile Disc-Recordable)[10].

3-Hydroxy -4-(2-hydroxy phenyl azo) naphthalene -1- Sulphonic acid (M.wt 366.33 gm/mole), (also called solochrome violet (Rs), see Schem 1) is an azo dye, used as metal indicator in the chelatometric determination of Al (III) in natural water[11,12]. In addition, Rs is a reactive azo dye belonging to the largest class of dyes commonly employed in textile industry[13]. No information is available about the spectrophotometric determination of La(III) with Rs reagent. In this present work, an attempt to adopt the reagent Rs as a chromogenic agent for a spectrophotometric determination of La(III) was done and the optimum reaction conditions for excellent metal ion sensitivities are evaluated.



Schem 1 : The molecular structure of Solochrome violet (RS)

Experimental

A Cintra 5 GBS Scientific equipment UV – Visible spectrophotometer , with 1 cm quartz cells and a Philips model PW-9421 pH-meter was used for the absorbance and pH measurements respectively.Infrared measurements were carried out on a Shimadzu-IR Prestege -ZI Fourier transform infrared.

Reagents

A stock (100 µg .ml $^{-1}$) solution of La(III) was prepared by dissolving 0.0117 gm of La_2O_3 purity (99.5%) (fluka) in 20 ml 5M HNO_3 and then diluted to 100 ml with distilled water Rs- Reagent purity (99.5%) (BDH) 2.72×10^{-3} M solution was prepared by dissolving 0.0996 gm in a 100ml distilled water by using a volumetric flask. Buffer solution (pH=10.0) was prepared by mixing 3.21 gm NH_4Cl with 2.24 gm KCl then 22.7 ml of NH_4OH was added and diluted to 100 ml with distilled water in volumetric flask[14], the pH being adjusted with a few drops of 0.5M NaOH or 0.5 M HCl.

Procedure for preparation of synthetic sample

Different water samples (Tap and river) were collected from various sites. The water samples were filtered through aWathman filter paper No 41. To 20 ml of each sample 0.0117 gm of La_2O_3 was added followed by addition of 20 ml of 5M HNO_3 and the mixture was heated with continous stirred until complete dissolution. The volume was then made to 100 ml with sample water . Test solutions were then prepared by subsequent dilution with the same water sample.

General Procedure

To various volumes of 7.198×10^{-4}M (100 µg. ml^{-1}) lanthanum (III) solution, 0.5ml of 2.72×10^{-3} M reagent and 0.5ml of buffer solution (pH=9.5) were added, then the resultant solutions were diluted to the 10ml with distilled water. The absorbance were measured at 459 nm against the reagent blank solution.

Results and Discussion

The ligand 3-hydroxy -4- (2-hydroxy phenyl azo) naphthalene -1-sulfonic acid reacts with La(III) to form a stable red-pink complex species, which is highly soluble in water. The absorption spectrum of the La(III)- reagent complex in aqueous solution was studied over the wavelength range 190-800 nm. The complex exhibited an absorption maximum at 459 nm against reagent blank (Fig.1).

Effect of pH

The effect of pH on the development upon the reaction between La(III) and reagent was studied at 459 nm. The pH being adjusted with a few drops of 0.5M HCl and 0.5M NaOH. A plot of absorbance against pH (Fig.2) ,showed that the absorbance was increased gradually as the pH increased and a maximum absorbance was obtained at the pH 9.50. The absorbance then decreased at pH value above 9.5, Hence a pH of 9.50 was used in all the subsequent experimental work.

Effect of reagent concentration

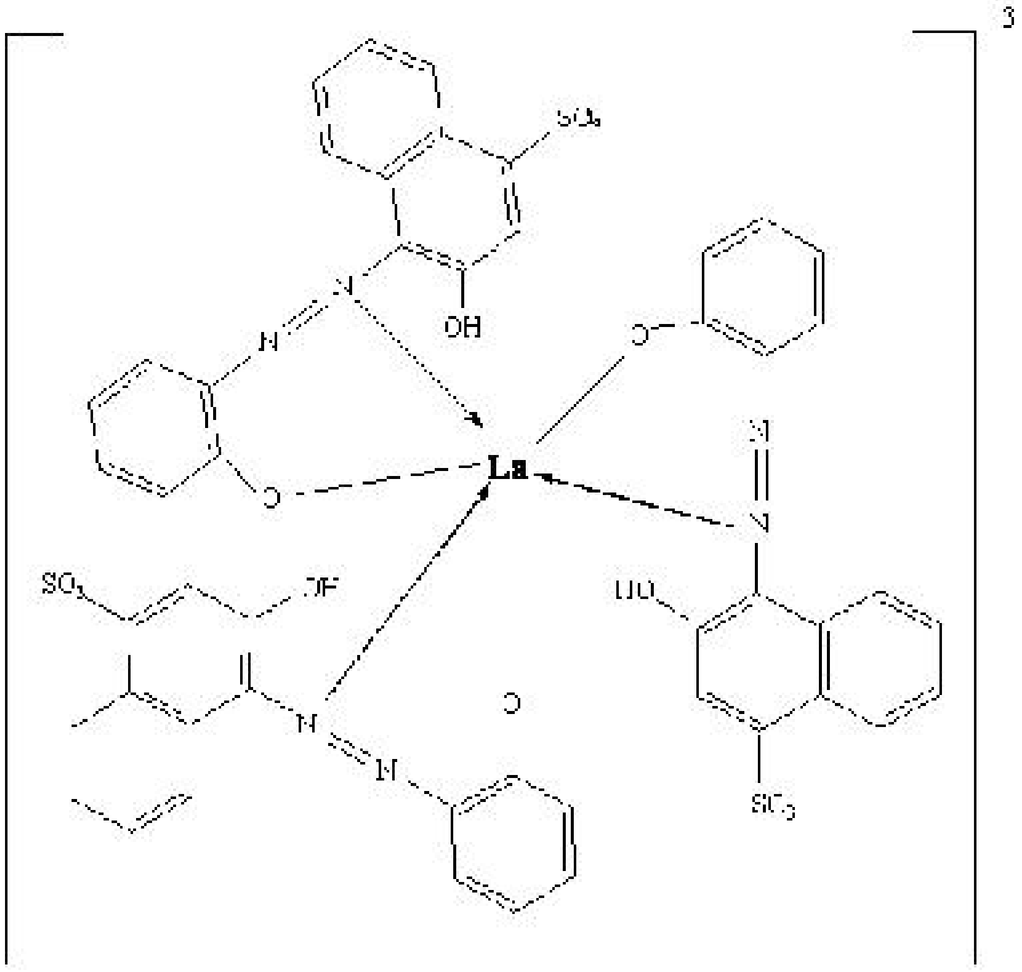
Various volumes (0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1 and 1.2 ml) of reagent solution were added to 6µg.ml^{-1} of La(III) solution, 0.5 ml of 2.72×10^{-3} M was found to be enough to develop the color to its fully intensity and a large excess of reagent solution has deleterious effect on the absorbance (Fig.3).

Effect of reaction time

The reaction is instantaneous, and the La(III)- reagent complex attained maximum and constant absorbance immediately after addition of the reagent and diluting the solution to the final volume. The color obtained remained strictly unaltered for at least 2 hours.

Stoichiometry of the complex

The stoichiometry of the complex has been studied by the mole ratio method . A series of solutions were prepared by transferring 1 ml aliquots of La(111) solution ($3.24\text{x}10^{-4}$) M , then increasing amount of reagent solution ranging from ($1.62\text{x}10^{-4}$ m mole-$1.45\text{x}10^{-3}$m mole) were added. To each solution 0.5 ml of buffer solution was added and the pH was adjusted to 9.50 with a few drops of 0.5 M HCl and for 0.5 M NaOH and the resulted solutions were diluted up to the 10 ml with distilled water . The absorbances were measured at 459 nm against the reagent blank solution. The obtained results are given in table (1) and fig (4) which shows that the ratio of La : Rs in the complex is 1:3, therefore a structure of the complex could be proposed as shown in scheme (2).



Scheme (2) : The proposed structure of the [La(III) – $(Rs)_3$ $]^{-3}$ complex.

The IR spectra of the ligand and complex (Fig 5, a and b) show sharp bands at 3417 and 1620 cm^{-1}, which can be attributed to the - OH and –N=N groups respectively. The band at 1620 cm^{-1} disappeared and a new band at 1404 cm^{-1} appeared while the band which corresponed to – OH group brodened, these indicate that the coordination in the formed charge transfer complex occur through the azo group and one of the hydroxyl group[15].

Calibration graph (Analytical data)

Under the optimum experimental conditions of the proposed method, a linear calibration graph was given and obtained between absorbance and concentration in the range given in (Fig. 6). The correlation coefficient, intercept and slope were calculated using least – square method .The mean Sandell's sensitivity and the apparent molar absorptivity values together with the limits of detection (D.L) and quantification (Q.L)[16] compiled in table(2), are indicative of the high sensitivity of the proposed method.

Method Validation

The accuracy of the method was evaluated by performing five replicate analyses on La(III) standard solutions at three different amounts of La(III) within the working range and calculating the percentage error. The precision was determined by calculating the relative standard deviations for five determinations at each level. (Table 3).

Effect of foreign ions

The effects of over 10 ions on the determination of 7 µg.ml^{-1} of La (III) were studied and the results are summarized in (Table 5).As can be seen, a large number of ions have no significant effect on the determination of La(III). On the other hand the most serious interferences were from Ce(III), Ho(III) and Pr(II) ions, so that prior separation would be essential.

Application to real samples

To evaluate the analytical applicability and to check the accuracy of the proposed method, the method was applied to the determination of La(III) in tap and river water spiked with La(III) (i.e synthelic samples) and the obtained result is summarized in (Table 6).

Conclusions

The present study described the use of solochrom violet (Rs) reagent for the development of selective , sensitive and accurate spectrophotometric methods for the determination of La (111) with (Rs) reagent, the acceptable –linearity and accuracy of the results indicated that the method can be applied for routine analysis of La(111) in real samples .

References

1. Henderson,P.(1984). Rare Earth Geochemistry, Elsevier, Amsterdam.p213-219.
2. Vijayan,S.; Melnky,A.J.; Singh,R.D.and Nuttall,K;(1989), Recovery of Lanthanides and Yttrium from red mud by selective leaching . Min. Eng. 41,p13-17.
3.Fthirlwall, F. (1982), A triple – Filament method for rapid and precise analysis of rare – earth elements by isotope dilution Chem. Geol. 35:155-166.
4. Jackobs,J.W.; Koritev,R.L.; Balchard,D.D. and Haskin.L.A. (1977), J. Radioanal. Inter ference from uranium in neutron activation analysis or rare – earths in silicate rocks. Chem. 40: 93-99 .
5.Date, A.R.and Gary,A.L. (1985), Determination of As, La, Bi and Hg in water samples by flow – injection inductively coupled plasma mass spectrometry with an- situ nebulizer , hydride generator .Spectrochim, Acta part B 40 :115.
6.Crock, J.G.and lichte,F.E. (1982), Determination of rare earth elements in geological materials by inductively coupled argon plasma / atomic emission spectrometry. Anal. Chem.. 54 :1329-1332.
7. Djingova,R.and Ivanova,J. (2002),Determination of rare earth elements in soils and sediments by inductively coupled plasma atomic emission spectrometry after cation – exchang separation. Talanta 57(5): 821-829.
8.Wang,S.; Shen,S. and Xu,H. (2000) Synthesis spectroscopic and thermal properties of a series of azo metal chelate dyes Pigments 44:195 .
9.Chapman, D.D.; Goswami, R. and Kovacs,C.A. (1995), Investigation of optical nonlinearities of azo nickel chelate compound by the z–scan technique. European Patent Application EP 0649884.
10.Park,H.; Kim,E.R.; Kim,D.J. and Lee,H. (2002), Optical properties of nickel(11) – azo complexes thin films for potential application as high – recordable optical recording media Bull. Chem. Soc. Japan 75, p2067 .
11.Brittain,H.C. (1979), Application of 8- hydroxyl quinoline –S- Sulfonic acid in the spectrophotometric determination of some lanthanides Anal. Chim. Acta, 106: 401.
12.Wang,X.; Lei,J.; Gan,S.; Bi. N. and wei,Z.(2001), Determination of the speciation of aluminum (111) in natural waters by adsorption stripping Voltammetry and complexation with A^{111} . solochrome violet RS Analytica Chimica Acta, Number 1:499.

13.Mrowetz,M. and Selli,E. (2005), Enhanced photocatalytic formation of hydroxyl radicals on fluorinated TiO_2. Phys. Chem .Chem. Phys; 7:1100.

14.Basavaiah,K. and Shakunthala,V. (2004), charan Ion- pair complexometric determination of cyproheptadine hydrochloride using bromophenol-blue. J of Science Asia 30: 163-170.

15- Silverstein, Robert M.; Bassler Clayton G. and Morrill, Terence C.(1981) ,Spectrometric Identification of Organic compounds .4_{th} Edition. John Wiley &Sons, USA.p318-322.

16- Siddappa,K.;Mallikkarjun,M.;Reddy,P.T.andTambe.M.(2008),Determination of La (III) by spectrohpotometric analysis Ecl.Quim, Saopaulo,33(4):41-46.

17-Fernandez L. and Olsina,R. (1990),Sensitive spectrophotometric determination of Lanthanum with 2 – (3,5-dichloro-2-pyrid(azo) -5-dimethylaminophenol). Analytical Sciences:Vol 6 (3): 112-121.

18- Guo Zien F.; Jiao Mai, Liang,P. and X. Bu. Lu.(1999), Study on the spectrophotometricDetermination of rare earths with a new chromogenic reagent . dibromo – p –Methyl- chlorosulfonazo- Chinese chemical letters 10 (10):851-854 .

19- Govinda ,P.; Mohan Reddy,K.P.; Krishna Reddy,V. and Raveendra Reddy.P.(2008), 2-Hydroxy – 1-naphthaldehyde-P-hydroxybenzoic hydrazone as a Spectrophotometric reagent for the determination of lanthanum(111) . Indion.J. Of chemistry. 47A :1381-1383.

20- Yadvendra,K. and Shrivastar.P.(1997), Solvent extraction spectrophotometric and Indvctively coupled plasma atomic emission spectroscopic determination of Lanthanum(111) with Crown hydroxomic acid. Tolanta, 45(2):397-404 .

21- Kokare ,B.N.; Han,S.H. and Amuse.M.A.(2009),Solvent extraction of lanthanum(111) byN – n- octylaniline from Salicylate media.Desalination and water treatment.12:79 – 86

Table (1) : Mole ratio method results

Conc. of reagent	$C_L:C_M$	Absorbance
1.62×10^{-5}	0.5	0.025
3.24×10^{-5}	1.0	0.070
4.90×10^{-5}	1.5	0.140
6.50×10^{-5}	2.0	0.180
8.09×10^{-5}	2.5	0.240
9.72×10^{-5}	3.0	0.290
1.14×10^{-4}	3.5	0.295
1.30×10^{-4}	4.0	0.291
1.45×10^{-4}	4.5	0.273

Table (2): Selected analytical parameters obtained with optimization experiments.

Parameter	Proposed method
Linear dynamic range ($\mu g.ml^{-1}$)	0.5-12
Intercept	0.0116
Slope	0.0531
Correlation coefficient (r)	0.9979
Molar absorptivity($L.mol^{-1}.cm^{-1}$)	7376.12
Sandell Sensitivity ($\mu g.cm^{-2}$)	0.0188
Detection limit * ($\mu g.ml^{-1}$)	0.475
Quantitation limit ** ($\mu g.ml^{-1}$)	1.440

$$* \text{ D.L} = \frac{3.3 \text{ x S.D of blank}}{\text{Slop of calibration curve}}$$

$$** \text{ Q.L} = \frac{10 \text{ x S.D of blank}}{\text{Slop of calibration curve}}$$

Table (3): Evaluation of accuracy and precision of the proposed method.

Amount of La(III) ($\mu g.ml^{-1}$)		(Error %)*	(R.S.D%)*
Taken	Found (mean)		
5.0	5.04	0.80	2.11
7.0	6.91	1.28	1.41
10.0	10.38	3.80	3.10

* for five determinations

Table (4): show the proposed method has acceptable linearity ranges when it compared with other method.

Table(4):Comparison of proposed method with other reported spectrophotometric methods.

Reagents	Beer's law limit $\mu g.\ ml^{-1}$	Ref.
2-(3,5-dichloro-2-pyridy(azo)-5- dimethyl amino phenol)	0.6-40	17
Dibromo-p-methyl – chlorosulfon-azo	1.0 – 15	18
2-Hydroxy-1-naphthaldihyde–p-hydroxybenzoic hydrazone	0.22 – 8.33	19
Crown hydroxamic acid	1.2 – 20	20
N-n – octyl aniline	0.45 – 18	21
3- hydroxyl-4- (2- hydroxyl-phenyl azo) naphthalene -1- sulfonic acid	0.5 – 12	This work

Table (5): Determination of 7 $\mu g.ml^{-1}$ of La(III) in the presence of foreign ions

Foreign ions	Amount added ($\mu g.ml^{-1}$)	Amount found ($\mu g.ml^{-1}$)	Error %
Cu^{+2}	0.50	7.08	+ 1.14
	1.20	7.11	+ 1.57
Cd^{+2}	0.50	7.14	+ 2.0
	2.90	7.09	- 1.28
Ni^{+2}	0.50	7.15	+ 2.14
	2.50	7.02	+ 0.28
Co^{+2}	1.50	6.91	- 1.28
	3.00	7.11	+1.57
Al^{+3}	0.75	7.09	+ 1.28
	1.00	7.05	+ 0.71
Cr^{+3}	0.75	7.06	+ 0.85
	1.00	7.10	+ 1.42
Mn^{+2}	0.70	7.09	+ 1.28
	1.25	7.11	+ 1.57
Zn^{+2}	0.70	7.11	+ 1.57
	1.25	7.15	+ 2.14
Ho^{+3}	0.70	7.30	+ 4.28
	1.50	7.52	+ 7.42
Ce^{+3}	0.70	7.20	+ 2.85
	1.50	7.39	+ 5.57
Pr^{+3}	0.70	7.22	+ 3.14
	1.50	7.15	+ 2.14

Table (6): Determination of La(III) added to a water samples $\mu g.ml^{-1}$.

Sample	Spiked	Measured	Recovery %
Tap water	4	3.80	98.0
	6	6.10	100.5
	8	8.80	102.5
River water	4	4.30	103.0
	6	6.40	102.0
	8	8.70	101.8

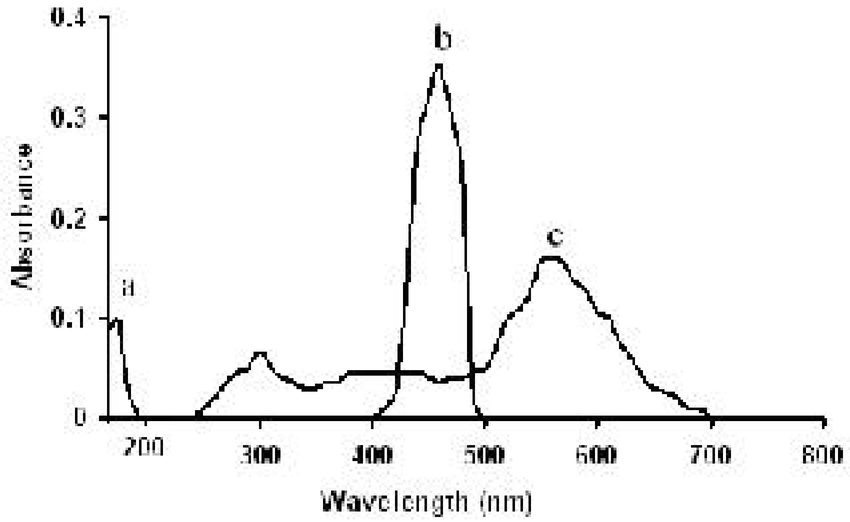


Fig.(1):Absorption Spectra of
a: 6 µg.ml^{-1} (La(III))
b: 6 µg.ml^{-1} La(III) (4.31x10^{-5} M),1.36×10^{-4}M (Reagent)at pH=9.50
c: blank 1.36 ×10^{-4}M (Reagent) at pH=9.50 against distilled water.

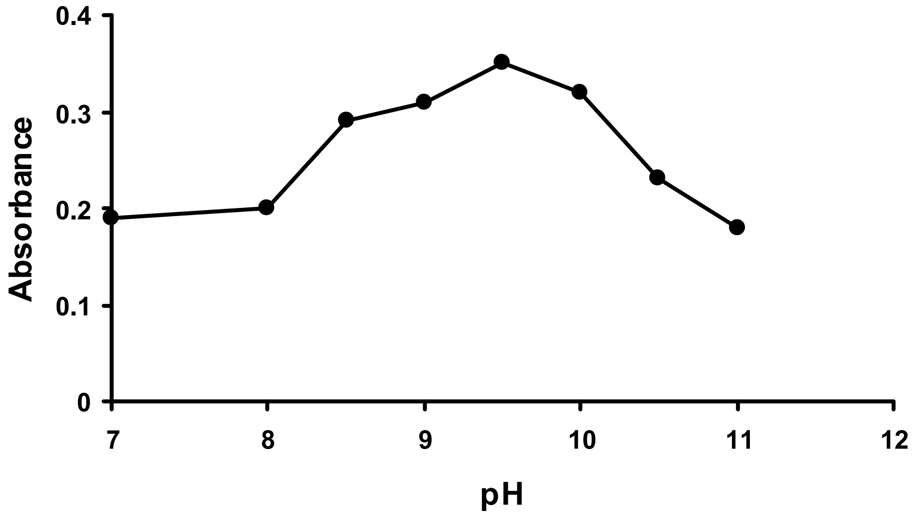


Fig.(2):Effect of pH on the absorbance of 6 µg.ml^{-1} La(III), 1.36 ×10^{-4}M (Reagent) at 459 nm.

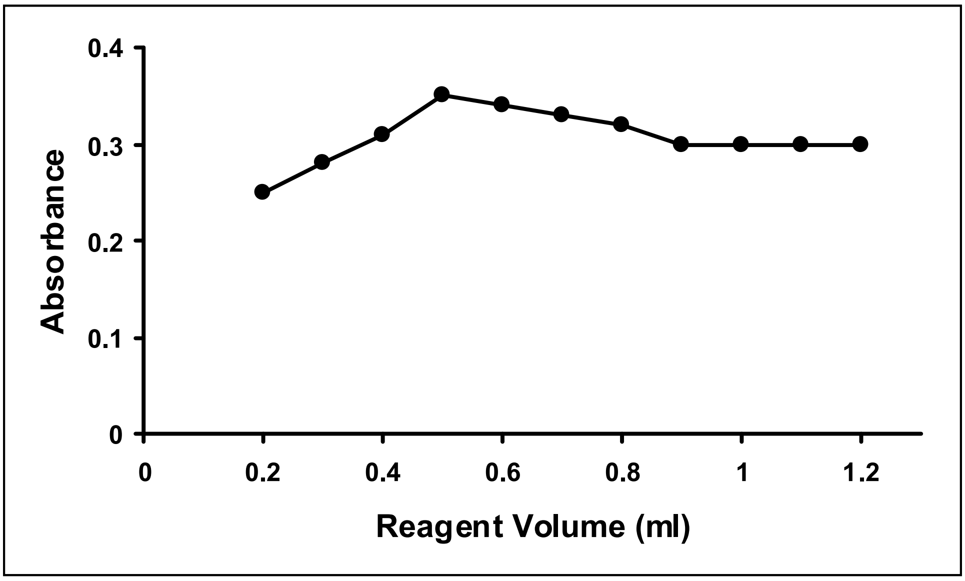


Fig.(3):Effect of reagent volume on the absorbance of 6 µg.ml^{-1} Lanthanum (III) solution.

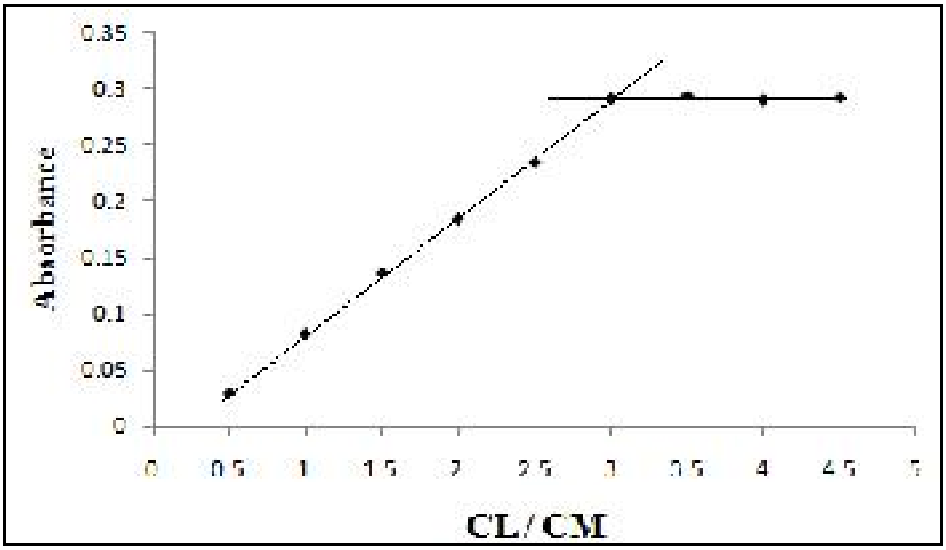
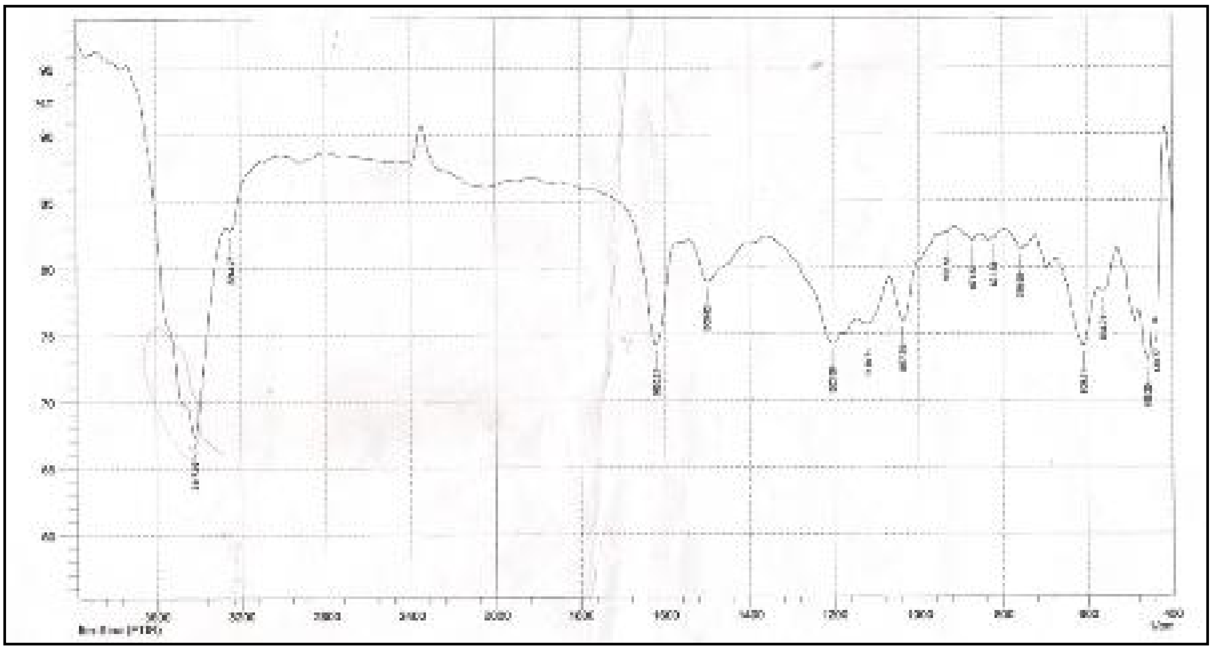
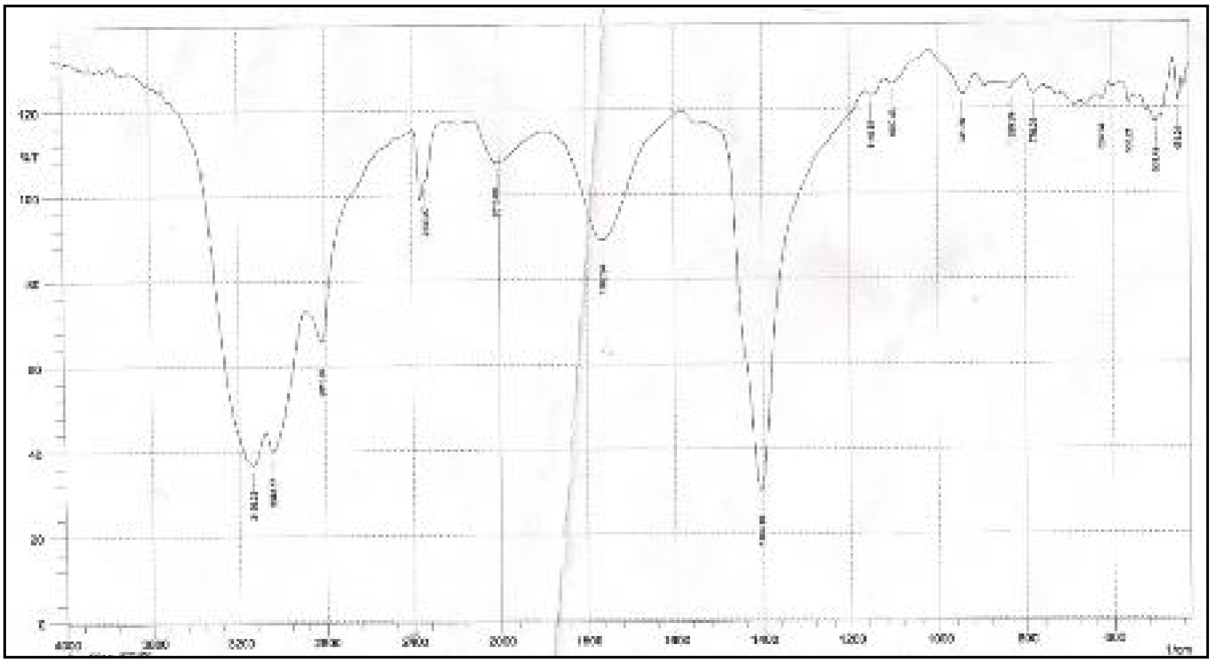


Fig.(4): Mole ratio plot of Lanthanum (III) determination by the proposed method.



Wavenumber 1/Cm

Fig.(5-a): IR Spctrum of the reagent



Wavenumber 1/Cm

Fig.(5-b):IR Spectrum of the La(III) – reagent complex

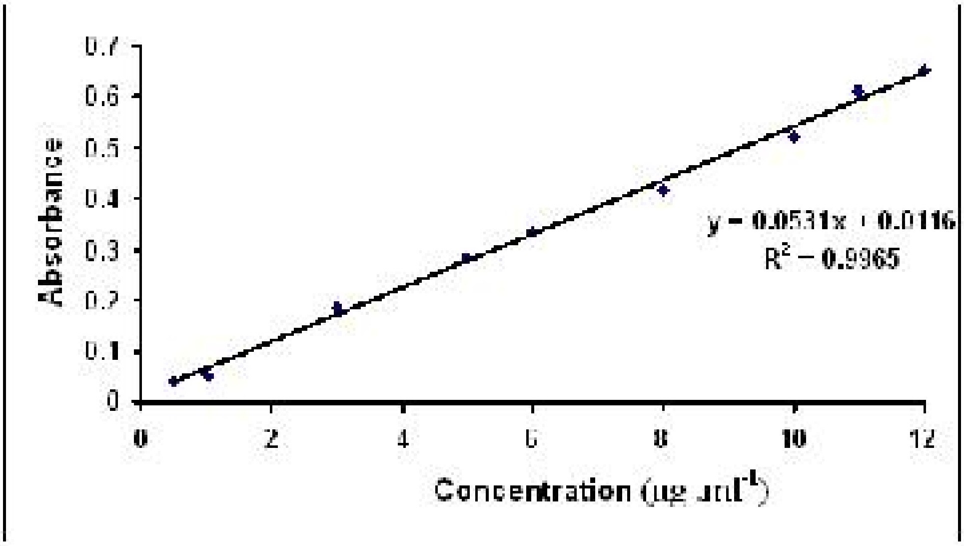


Fig. (6) : Calibration graph

طريقة طيفية جديدة لتقدير اللانثانوم (111) باستخدام كاشف 3- هيدروكسي -4- (2- هيدرروكسي فنيل ازو) نفثالين -1- حامض السلفونيك

استلم البحث في:27 حزيران2010

قبل البحث في :9 تشرين الثاني2010

سمر احمد درويش ، ازهار صادق حمودي ، رؤى مؤيد محمود

قسم الكيمياء ، كلية التربية – ابن الهيثم ، جامعة بغداد

الخلاصة

اقترحت طريقة طيفية بسيطة وسريعة وحساسة لتقدير اللانثانوم (111) باستعمال 3- هيدروكسي -4-(2 – هيدروكسي فنيل ازو) نفثالين -1- حامض السلفونيك كاشف لوني تعتمد الطريقة على تكوين معقد بلون احمر ارجواني نتيجة لتفاعل (111) La مع الكاشف في وسط قاعدي $pH = 9.5$ الذي اظهر اعظم امتصاص عند طول موجي مقداره 459 نانوميتر . لقد اظهرت الطريقة انطباق قانون بير لمدى من التراكيز يتراوح بين (0,5 –12) مايكروغرام . مل $^{-1}$ وكانت قيمة حساسية ساندل تساوي 0.0188 مايكروغرام .سم $^{-2}$ ، وكان معامل الامتصاص المولي يساوي 7376.12 لتر .مول$^{-1}$.سم$^{-1}$ المعقد المتكون بنسبة 1:3 (فلز : كاشف). لقد تمت دراسة تاثير وجود متداخلات مختلفة في تقدير (111) La بتطبيق الطريقة تحت الظروف المثلى .

الكلمات المفتاحية :المطيافية ، تعيين(La) ، هيدروكسي فنيل ازو